GAS PHASE POLYMERIZATION OF ETHYLENE

By

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PREFACE

Producers of commodity plastics such as polyethylene are in a constant search for new methods to make the plastic. An atmospheric and solvent free process would be a welcome new addition. This study presents the results of gas-phase experiments carried out at approximately 18 psia and 20°C to 174°C. Both nickel oxide and molybdena catalysts were studied.

I am indebted to Dr. Billy L. Crynes who provided advice and guidance while serving as my adviser during this research project. Mr. Eugene McCroskey, laboratory technician, deserves a special thanks for his many helpful contributions. I wish to thank Mr. Carl W. Orrick, graduate student, for the analysis of the ethylene gas.

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CHAPTER I

INTRODUCTION

The description of a basic commercial process is a necessary step to understanding changes made to the process. Briefly, a commercial ethylene polymerization process involves: (a) activating a catalyst to the required valence state, (b) placing the catalyst in a reactor and filling the reactor with solvent, (c) saturating the solvent with ethylene and raising the temperature and pressure of the reactor to the desired levels.

The solvent for a commercial process serves several functions. It acts as a medium to carry ethylene gas monomer to catalyst sites for reaction and as a carrier to remove polymerized material from the catalyst. Also the heat of reaction is dissipated by the solvent.

A solvent also has several disadvantages. The solvent is a major source of catalyst poisions. Water, oxygen, sulfur, etc., must be reduced to parts per million (ppm) levels to prolong catalyst activity. The solvent purification is therefore a major cost of the process. Recovery of product from the solvent is another problem associated with the solvent. Also pressures much higher than atmospheric are necessary to maintain the necessary quantities of ethylene in solution.

The solvent further clouds the process by making mechanistic studies more complex. In addition to the general reaction steps of initiation, propagation, and termination, some account must be made for

radical transfer to solvent as well as monomer. The exact mechanism by which the reaction takes place is open to considerable question. Clark and Bailey (4) present two theories on the polymerization mechanism. Katz and Saidel (12) and Friedlander and Resnick (9) also develop several models for the reaction. The effect of a solvent on the catalyst activity is also open to some question.

One method of simplifying mechanistic studies would be the use of a gas phase process, i.e., conversion of ethylene to products without the presence of a solvent. A simplified model, such as follows, would more closely represent the reaction of a gas phase process.

$$\text{Initiation} \quad R^{\cdot} + M \xrightarrow{k_I} M_1^{\cdot} \tag{1-1}$$

$$\text{Propagation} \quad M_1^{\cdot} + M \xrightarrow{k_p} M_x^{\cdot} \tag{1-2}$$

$$M_x^{\cdot} + M \xrightarrow{kp} M_{x+1}^{\cdot}$$

$$\text{Termination} \quad M_x^{\cdot} + M_y^{\cdot} \xrightarrow{k_t} M_{x+y} \tag{1-3}$$

where $R^{\cdot}$ represents a free radical on the catalyst, M represents the ethylene monomer, $M^{\cdot}$ is a polymer chain with a free radical, the x and y subscripts refer to two different growing polymer chains, M_{x+y} is the combination of the two growing chains, and k_I, k_p, and k_t indicate the rate constants for the steps of initiation, propagation, and termination respectively. The fact that this is only one model for the reaction should again be emphasized.

Initial studies of the gas-phase processes should be limited to determining the conditions for which the reaction will occur. Literature sources (1,2,14,15,17,21) have reported a wide range of conditions for the actual polymerization reaction. This study was concerned with

finding the extent of reaction possible for low temperature ranges (20° to 175°C), at essentially atmospheric pressure, and for selected catalysts.

CHAPTER II

LITERATURE

During the years of 1953-57, after the advent of high density polyethylene, several articles were published describing methods for making the polymer (9). A greater quantity of facts was published in patents concerning the high density process. In almost all of the early patents mention was made that polymerization could be effected at atmospheric pressure, without the use of a solvent or liquid medium.

Standard Oil of California has several patents (13,14,16,21) which indicate that high density polyethylene can be formed at atmospheric pressure with a molybdena or nickel catalyst, and without a solvent. One patent (13) is devoted specifically to the gas-phase polymerization of ethylene. In the gas phase patent, a flow scheme is presented for a typical commercial gas-phase polymerization process (Figure 1). The gas phase system was designed primarily for the recovery of gasoline products; however, the polymer possibilities should not be overlooked. The catalyst suggested for this process was a nickel or cobalt type supported on activated carbon. Ethylene is fed down-flow through a fixed bed reactor. To recover the solid products from the reactor, the bed of catalyst is washed with a solvent. Using two reactors prevents down time for the system. The gas phase system does not show great detail for the purification of the high molecular weight polymers.

Comparison of the above gas phase process with a commercial

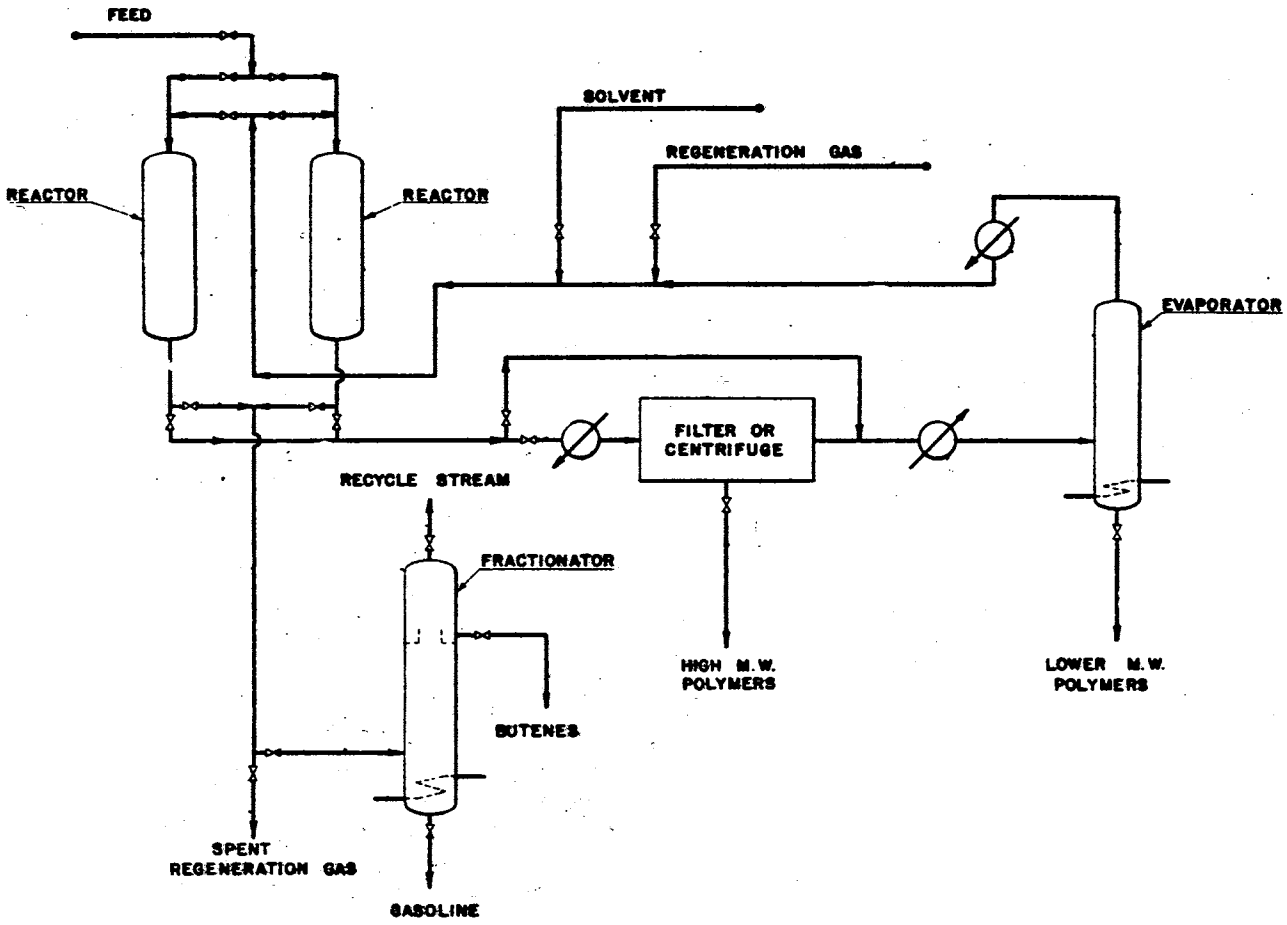

Figure 1[13]. Ethylene Polymerization in the Vapor Phase

Phillips solution process (Figure 2) shows some simplification for the gas phase process. The necessity of a high purity solvent is eliminated in the gas phase process.

Others have patented processes for the gas phase ethylene polymerization using a Ziegler type catalyst (17,19). Also among the early gas phase experiments are some on chromia type catalysts (5).

Initial literature search indicated that the most detailed information was on catalysts of molybdena and nickel. Much of the information was primarily concerned with a solvent type polymerization process; however, conditions for a gas phase process were also given. Catalyst activation was identical for either the solvent phase or the gas phase process. The ranges on the reported experimental conditions for the catalyst activation and polymerization are listed in Table I. The

TABLE I (11,13,14,15,21)

RANGE ON CATALYST ACTIVATION AND POLYMERIZATION CONDITIONS

Catalyst		Time	Temperature	Pressure
1-5% Ni on activated carbon	Activation	30 min. to 2 hours	200-400°C (392-752°F)	200 to 2000 psig
Size: 1/16" pellets to powder	Reaction	15 min. to 3 hours	from below room to 200°C (392°F)	0 to 5000 psig
5-34% Mo on γ-alumina	Activation	30 min. to 16 hours	400-500°C (752-932°F)	0 to 3000 psig
Size: 1/8 by 1/8" pellets to powder	Reaction	30 min. to 10 hours	75 - 300°C (167-572°F)	0 to 5000 psig

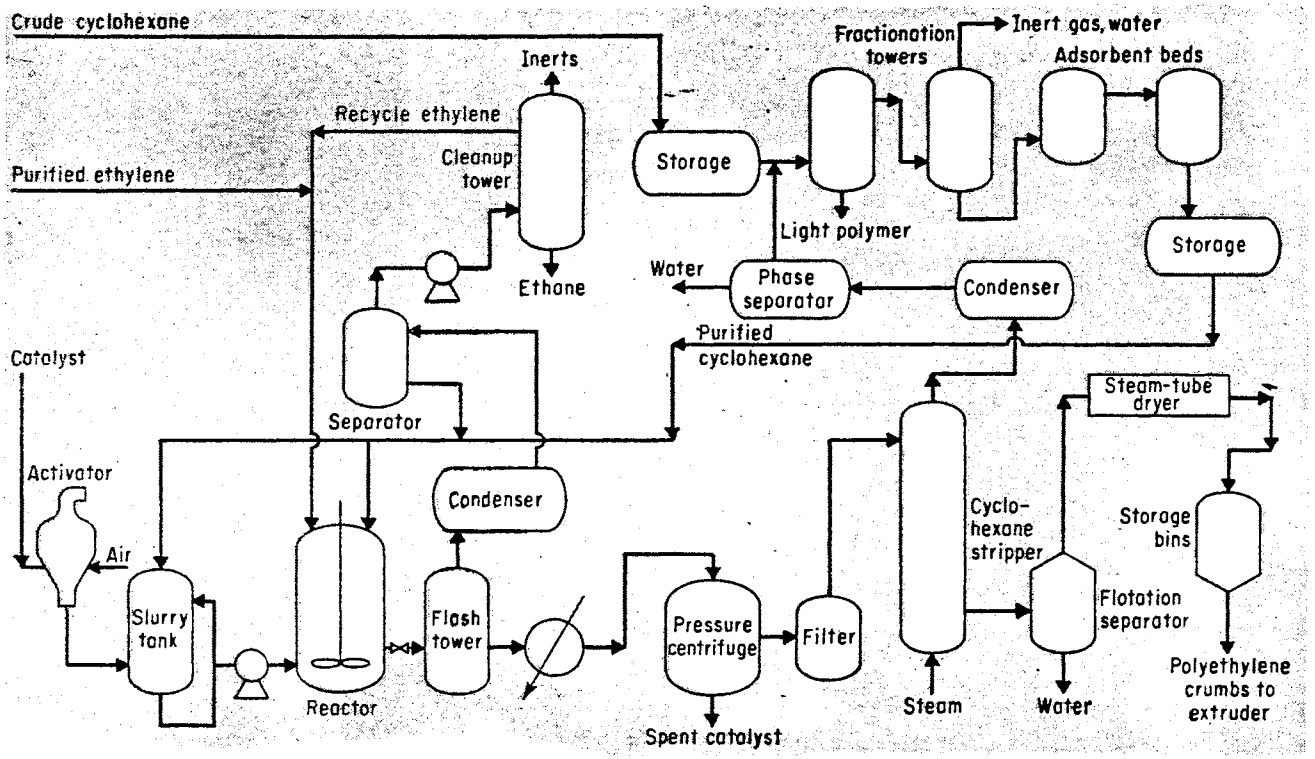

Figure 2[1]. Polyethylene Process of the Phillips Petroleum Company

conditions tabulated are applicable to both the gas phase and solvent type processes. Suggested operating conditions are listed in Table II.

TABLE II

SUGGESTED CATALYST ACTIVATION AND POLYMERIZATION CONDITIONS

Catalyst		Time	Temperature	Pressure
5% Ni on activated carbon	Activation	30 min.	230°C (626°F)	75 psig
Size: 6 to 14 mesh	Reaction	1 hour	120°C (248°F)	2000 psig
8% Mo on γ-alumina	Activation	1 hour	460°C (860°F)	150 psig
Size: 2 to 6 mesh	Reaction	3 hours	130°C (266°F)	1100 psig

The suggested conditions for polymerization (Table II) were actual conditions for a particular study (13,21).

The polymerization of ethylene is exothermic and therefore presents some problems in maintaining proper temperature control. For best temperature control, a fluidized bed reactor has been suggested (14). Batch type reactors, however, can be used with equal success as evidenced by present commercial processes (1,2).

Pressure was considered necessary to maintain a sufficient concentration of ethylene in the liquid solvent (15). Higher concentrations of ethylene would help overcome any liquid film resistance about the catalyst particle. Discussion of a resistance, however, was not within

the scope of the publication.

The effect of catalyst particle size was another point open to some speculation. For nickel on carbon, a particular particle size was suggested by one article (13), but the statement that yield of polymer was unaffected by particle size was made in another (15). The specific viscosity, however, was shown to be a function of catalyst particle size (15). The yield of polymer from a molybdena catalyst seemed to be independent of particle size, although the activation time for the catalyst was a strong function of the size (21).

Another factor to be considered for both catalysts was the poison level. Oxygen and water were the major poisons and allowable levels were said to lie between 10 parts-per-million (ppm) and 2000 ppm for the oxygen and up to .5% for the water.

CHAPTER III

EXPERIMENTAL

Investigation of the gas phase process began with the specification of reaction conditions. The temperature range of 20° to 175°C was chosen to determine the lowest temperature at which the process could be effected. The pressure of 18 psia was chosen for the potential commercial economic advantages of a near atmospheric process. Reaction time was chosen as three hours as suggested from the literature.

Specification of catalyst size and activation conditions was also necessary. A choice of catalyst particle size of 20 to 48 mesh was based on promoting good fluidization. Various combinations of oxidation and reduction were used on both catalysts to find the most active state. Activation temperature and pressure were varied for the nickel catalyst to find the best method for activation. Temperature and pressure were held constant for the molydena catalyst since activation conditions were more accurately specified in the literature.

Equipment

The reaction system was constructed as shown in Figure 3. (See Table III for a complete listing of the equipment.)

The volume of the system and the pressure drop caused by piping were both important. The actual volume of the system should be kept to a minimum to reduce the time necessary to remove impurities from the

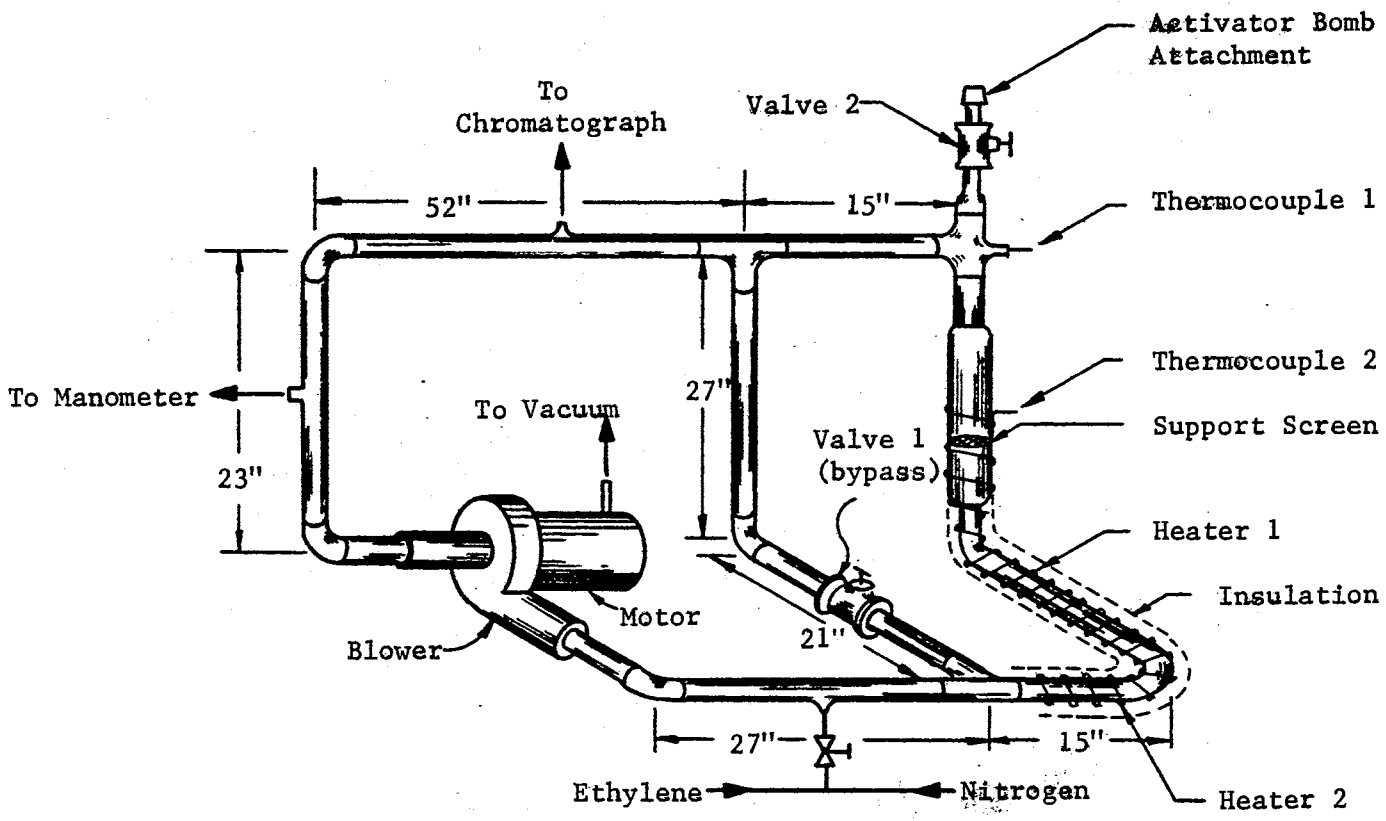

Figure 3. Reaction System

TABLE III

LIST OF REACTION SYSTEM EQUIPMENT

Pipe -- 1½" I.D., galvanized steel
Reactor -- 2" I.D., pyrex glass, 15" long
Valve 1 -- 1½" gate valve, Brass-125 psia max.
Valve 2 -- 3/4" gate valve, brass-300 psia max.
Blower -- 8" diameter, cover constructed of 1/16" sheet iron
Motor -- G.E., 1/2 horsepower, explosion proof
Heater 1 -- 96" heavy insulated heating tape, 768 watts
Heater 2 -- 6 foot Marsh beaded heater, No. 3116-2
Manometer -- 8" Meriam manometer
Thermocouple 1 -- Conax, bare end, copper-constantan
Thermocouple 2 -- Conax, shielded grounded end, iron-constantan
Potentiometer -- Leeds & Northrup Co. No. 8690
Vacuum Pump -- Duo-Seal
Support Screen -- 48 Mesh stainless steel
Insulation -- 1" wide asbestos tape
Tubing to bottled gases, chromatograph, and manometer -- 1/4" O.D., copper

system. The minimum volume for this study was dictated by the type blower involved. Smaller transfer lines caused higher pressure drops and the blower used in the system could overcome a maximum pressure drop of only a few inches of water. The system should also be air tight since oxygen is a primary catalyst poison and small quantities can have a ruinous effect on the reaction (14,15).

Ethylene was recirculated via the blower and the flow through the catalyst bed was controlled by the amount of gas bypass allowed by the bypass valve. To drive the blower, a commercial explosion-proof motor was sealed inside the reaction system. The motor was wound with copper tubing to provide adequate cooling in the enclosed system. By enclosing the motor in the system, leakage around the motor shaft was eliminated. To avoid danger from the motor, oxygen must be removed from the system before filling with ethylene.

To define temperature effects, the gas in the system was heated with a heating tape on the exterior of the reactor and piping. A greater range on catalyst bed temperature could have been obtained by heating and insulating more sections of the system. The amount heated and insulated for this study was adequate for the temperature range desired. The temperature of the gas in the system was measured by a thermocouple placed just above the glass reactor tube (Figure 4). The reactor wall temperature was measured by placing a thermocouple between the heating tape and the glass wall of the reactor.

For catalyst activation, a tubular bomb was constructed. The bomb was a length of stainless-steel tube. The tube was threaded and a gate valve was screwed onto one end and a globe valve was screwed to the other. The bomb was connected to gas bottles via 1/4" copper tubing

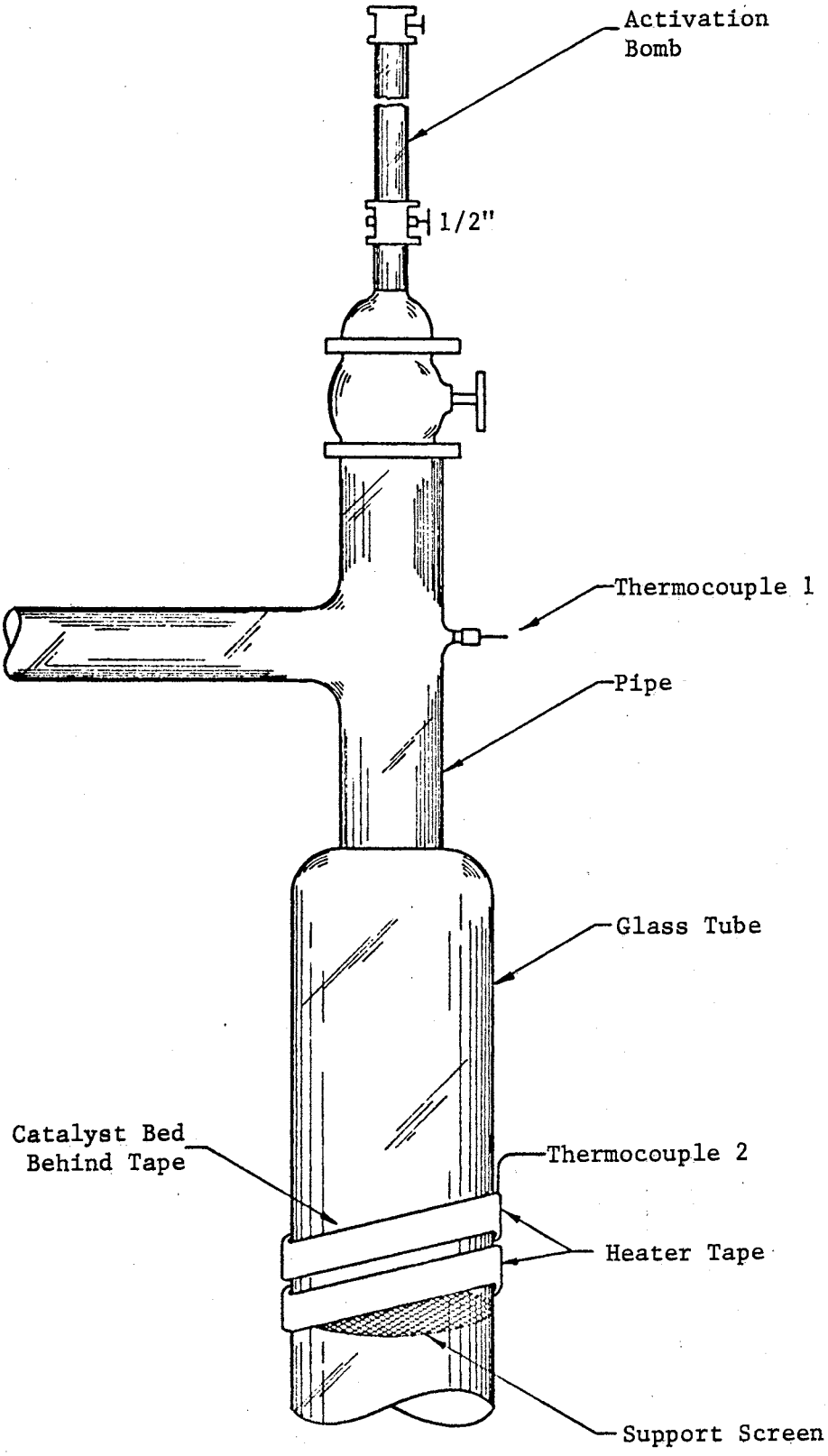

Figure 4. Location of Thermocouples

as shown in Figure 5. Materials of construction for the bomb and the activation system are listed in Table IV. The bomb was heated by plac-

TABLE IV

EQUIPMENT LIST FOR ACTIVATION APPARATUS

Pipe -- 1/2" I.D. - 304 stainless steel, 15" long
Valve 1 -- 1/2" gate valve, brass, 300 psia max.
Valve 2 -- 1/2" globe valve, brass, 300 psia max.
Heater -- 750 watt, heavy duty combustion furnace, single zone
Tubing to bottled gases -- 1/4" O.D., copper

ing it lengthwise in a Multiple Unit Heater. The temperature of the catalyst was determined by a thermocouple in the center of the bomb, which corresponded to the center of the heater. The thermocouple was manually inserted through the open end of the activation tube and the temperature measured in the radial center of the tube avoiding touching the walls.

Procedure

Reactor Preparation and Operation

A description of a typical run follows, beginning with a careful procedure for filling the system with ethylene. The reaction system was evacuated to 10 psia internal pressure with a Duo-Seal vacuum pump, then filled to atmospheric pressure with dry nitrogen gas. (See Table V for list and specifications of gases used.) After the evacuation-filling procedure was repeated ten times the system was pressured up to

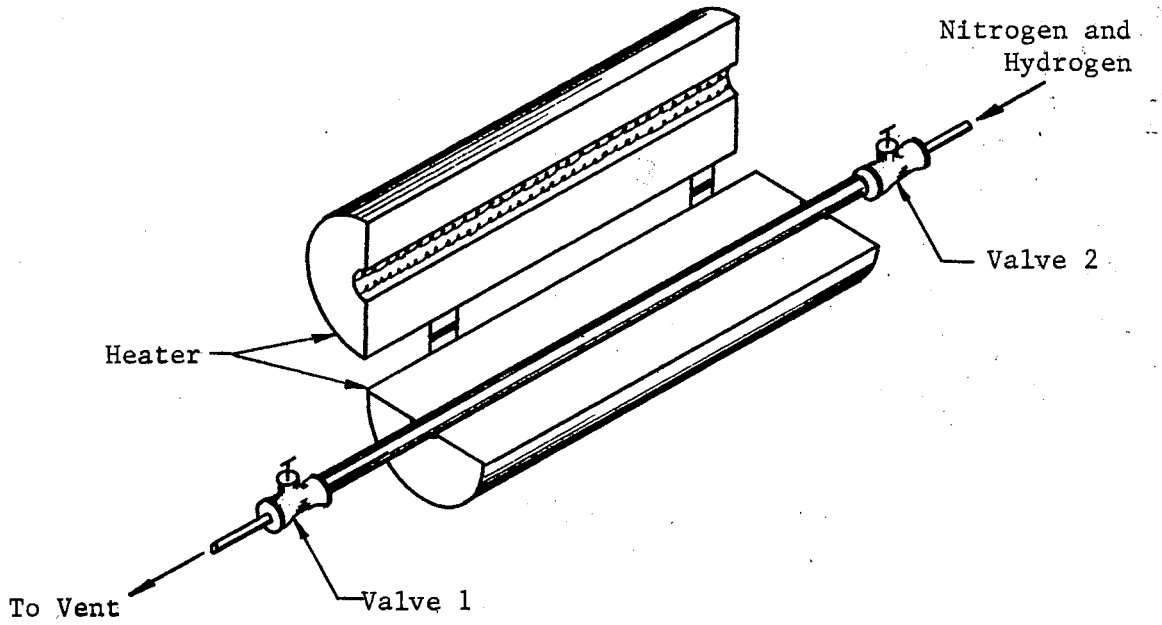

Figure 5. Activator Bomb and Heater

18 psia and dry nitrogen was purged through the vacuum pump for five minutes. The system was next evacuated to 10 psia and filled with ethylene. The evacuation-filling procedure was carried out five times with ethylene. The system was then pressured up to 18 psia and a line leading to a chromatograph was allowed to purge for one minute. A sample of the gas was analyzed on an F&M Model 500 chromatograph. Complete details of the chromatograph and its operation are given in the Appendix. The evacuation-filling was continued five more times with ethylene as the make-up gas. Again the sample line was purged for one minute and a sample of the gas analyzed in the chromatograph. After the ten ethylene evacuations the system was pressured up to 18 psia and purged for five minutes. Another chromatogram of the contents of the system was made. See the Appendix for sample chromatogram and calculations. During the filling process the gas in the system was simultaneously being heated to approximately 110°C. The reactor system was then maintained with ethylene at 18 psia while the catalyst was activated.

TABLE V

LIST OF GASES AND CATALYSTS

Hydrogen -- 99.95%, prepurified -- Matheson
Helium -- 99.995%, prepurified -- Airco
Nitrogen -- 99.99%, prepurified -- Airco
Ethylene -- 99.8%, pure grade -- Phillips
Nickel Catalyst -- 10-12% Nickel Oxide on Gamma Alumina -- Girdler T-310
Molybdena Catalyst -- 10-12% Molybdic Oxide on Gamma Alumina -- Girdler T-306

The reaction and shut down procedures were simple. For reaction the bed of catalyst was fluidized by the flowing ethylene, and for most runs, the ethylene was contacted with the catalyst for three hours. The system was shut down by purging 15 minutes with nitrogen.

The final run with the molybdena catalyst was a batch run made in the activator bomb. The catalyst was activated in the previously described fashion. For polymerization, the temperature was dropped to approximately 150°C, the activator bomb was filled with ethylene, and the pressure raised to 165 psig. A small amount of ethylene was added to the system to maintain the pressure constant. The reaction was allowed to proceed for three hours. The products were then removed from the activation tube and analyzed, as described below.

Catalyst Activation and Transfer

Activation of the catalyst in the bomb and transfer to the reaction system were the next concerns. The catalyst to be used in the run was heated to the desired temperature in the activator bomb. A constant flow of dry nitrogen passed through the bomb during heat up time. Heat up time for the bomb was usually one hour. Next, the catalyst was reduced with hydrogen for some specified length of time. At the end of the reduction time the activation tube was closed on one end and pressured to 150 psig with hydrogen. The activator was removed from the heater and screwed onto the polymerization apparatus (as shown in Figure 4). The valve between the activator and the reactor was opened and the system was purged for five minutes with ethylene to insure no additional oxygen from the dead space between activator bomb and reactor was added to the polymerization system. Another chromatogram was run

as a check on impurity level. The final valve between catalyst and reactor was opened and the catalyst allowed to fall onto the catalyst support screen in the reaction tube. The polymerization system was closed except for a very small ethylene addition to maintain the system's operating pressure.

Analysis

Determination of the amount of ethylene converted to polymer was the last step to completing a run. To determine the conversion of ethylene to polymer, the catalyst was first boiled in chloroform. The hot chloroform was then poured into dishes for evaporation. The catalyst was next boiled in benzene and the benzene was also poured into dishes for evaporation. The resinous material left in the dishes was weighed to determine the amount of ethylene converted. While boiling, sufficient solvent to cover the catalyst 1/2" was used. Evidence that there had indeed been some conversion was the main pursuit in the washing process.

CHAPTER IV

RESULTS

Nickel Catalyst

Table VI shows the conditions studied for the nickel on alumina. The effects of temperature, catalyst activation, and poison level were the primary variables studied.

Activation temperatures of 260°, 330°, and 360°C were used (with the exception of runs 12-N and 13-N), with activation pressures of 14.7 psia and 200 psig. Various combinations of oxidation (heating in air) and reduction (heating in H_2) were also considered during activation. Oxidation varied from none to two hours and reduction from 15 minutes to 4 hours. Runs 3-N, 5-N, 12-N, and 13-N resulted in an active catalyst.

Reaction temperatures of 20°C to 175°C were studied. This range of temperatures fell within the suggested reaction temperature limits. Two and three hours were the reaction times considered. The reaction pressure of 3 to 4 psig was held low to determine the extent of reaction which could be effected at essentially atmospheric pressure. The runs which resulted in an active catalyst also gave some conversion upon polymerization. The conversion, however, was quite low (about .03 gm per 38 gm catalyst).

TABLE VI. RESULTS OF EXPERIMENTS WITH NICKEL

Catalyst	Run No.	Activation			Reaction				
		Time	Temperature	Pressure	Time	Temperature	Pressure	Particle Size	Comments
10 - 12% Nickel Oxide on γ-Alumina	1-N	1.5 hr Air 1.5 hr H_2	330°C	14.7 psia	2 hr	20°C external (20°C internal)	3.3 psig	20 to 48 mesh	Catalyst mostly grey. No product
	2-N	2 hr Air 1 hr H_2	260°C	14.7 psia	2 hr	77°C external (35°C internal)	3.3 psig	20 to 48 mesh	Catalyst mostly grey. No Conversion.
	3-N	2 hr Air 1 hr H_2	360°C	14.7 psia	2 hr	85°C external (40°C internal)	3.7 psig	20 to 48 mesh	Catalyst grey-green mixture. Low conversion.
	4-N	2 hr Air 45 min H_2	360°C	14.7 psia	2 hr	88°C external (40°C internal)	4.0 psig	20 to 48 mesh	Catalyst black and green. No conversion.
	5-N	1 hr N_2 40 min H_2	260°C	200 psig	2 hr	120°C external (55°C internal)	3.5 psig	20 to 48 mesh	Catalyst grey-green mixture. Low conversion.
	6-N	1 hr N_2 40 min H_2	260°C	14.7 psia	2.5 hr	190°C external (80°C internal)	3.0 psig	20 to 48 mesh	Catalyst mostly grey. Regenerated Run 5. No product.
	7-N	2 hr Air 40 min H_2	260°C	14.7 psia	2 hr	190°C external (80°C internal)	3.5 psig	20 to 48 mesh	Catalyst mostly grey. Regenerated Run 5 and 6. No product.
	8-N	1 hr N_2 45 min H_2	260°C	200 psig	1.5 hr	370°C external (104°C internal)	7.5 psig	20 to 48 mesh	Catalyst grey-green and black. Questionable conversion.
	9-N	1 hr N_2 45 min H_2	260°C	200 psig	3 hr	400°C external (115°C internal)	3.5 psig	20 to 48 mesh	Catalyst black-green. No conversion.
	10-N	1.5 hr Air 1 hr H_2	260°C	14.7 psia	3 hr	385°C external (107°C internal)	3.0 psig	20 to 48 mesh	Catalyst black and green. No conversion.
	11-N	1 hr N_2 4 hr H_2	260°C	200 psig	3 hr	385°C external (110°C internal)	3.0 psig	20 to 48 mesh	Catalyst mostly black. No conversion.
	12-N	35 min heat up in H_2	unknown (max of 200°C)	14.7 psia	3 hr	385°C external (110°C internal)	3.5 psig	20 to 48 mesh	Catalyst grey-green mix. Low conversion. Catalyst turned more green during reaction.
	13-N	15 min heat up in H_2	unknown (max of 180°C)	14.7 psia	3 hr	385°C external (110°C internal)	3.5 psig	20 to 48 mesh	Catalyst grey-green mix. Low conversion. Catalyst turned more green during reaction.

Molybdena Catalyst

Table VII shows the conditions studied for the molybdena catalyst. The variables considered for the molybdena system were reaction temperature, pressure, poison level, and catalyst activation.

The activation temperature was held between 430° and 480°C as suggested in the literature (Table II). Activation pressure was held at 200 psig with the exception of Run 4-M. The main variable for activation was the oxidation and reduction time. An active catalyst was produced with reduction times from five mintues to 1 hour. Total oxidation or total reduction, Runs 4-M and 5-M respectively were the runs which failed to give an active catalyst.

The reaction time was held at three hours for all runs except Run 2-M. For the first nine runs the pressure was held between three and four psig to determine if polymerization would occur at low pressure. The gas temperature for the first nine runs was between 90° and 175°C. The result of increasing the temperature was a lower molecular weight product. The conversion for the first nine runs was very low (about .03 gm/38 gm catalyst) except for Runs 4-M and 5-M where no conversion was obtained.

For Runs 10-M and 11-M, pressure of 165 psig was used. The temperature and time were similar to the first nine runs, but more conversion was obtained from Run 10-M (about 3 gm/38 gm catalyst). The temperature of 455°C on Run 11-M was outside the range for polymerization suggested by the literature (Table I), and no conversion was obtained.

TABLE VII. RESULTS OF EXPERIMENTS WITH MOLYBDENA

Catalyst	Run No.	Activation				Reaction				
		Time	Blanket Gas	Temperature	Pressure	Time	TTemperature	Pressure	Particle Size	Comment
10 - 12% Molybdic Oxide on γ -Alumina	1-M	Heat up 1 hr 10 min purge 50 min activation	N_2 H_2 H_2	430° to 480°C	200 psig	3 hr	290°C external (95°C internal)	3.5 psig	20 to 48 mesh	Very low conversion. High molecular weight.
	2-M	Heat up 1 hr 10 min purge 35 min activation	N_2 H_2 H_2	430° to 480°C	200 psig	3.5 hr	270°C external (90°C internal)	3.5 psig	20 to 48 mesh	Very low conversion. High molecular weight.
	3-M	Heat up 1 hr 10 min purge 40 min activation	N_2 H_2 H_2	430° to 480°C	200 psig	3 hr	370°C external (104°C internal)	4 psig	20 to 48 mesh	Very low conversion. High molecular weight.
	4-M	Heated 2 hr in air	Air	430° to 480°C	14.7 psia	3 hr	400°C external (175°C internal)	3.5 psig	20 to 48 mesh	No conversion.
	5-M	Reduced in H_2 4 hours	H_2	430° to 480°C	200 psig	3 hr	380°C external (175°C internal)	3.5 psig	20 to 48 mesh	No conversion.
	6-M	Heat up 1 hr 15 min activation	N_2 H_2	430° to 480°C	200 psig	3 hr	385°C external (175°C internal)	3.5 psig	20 to 48 mesh	Very low conversion. Some greasy prod. (lower mol. wt.)
	7-M	Heat up 1 hr 5 min activation	N_2 H_2	430° to 480°C	200 psig	3 hr	385°C external (177°C internal)	3.5 psig	20 to 48 mesh	Very low conversion. Greasy product. (lower mol. wt.)
	8-M	Heat up 1 hr 35 min activation	N_2 H_2	430° to 480°C	200 psig	3 hr	380°C external (174°C internal)	3.5 psig	20 to 48 mesh	Very low conversion. Greasy prod.
	9-M	Heat up 1 hr 1 hr activation	N_2 H_2	430° to 480°C	200 psig	3 hr	370°C external (135°C internal)	3.5 psig	3/16 x 3/16" Tablets	Very low conversion. Greasy product.
	10-M	Heat up 1 hr 1 hr activation	N_2 H_2	430° to 480°C	200 psig	3 hr	130° to 160°C	165 psig	20 to 48 mesh	Good conversion. Both high and low Mol. wt. product.
	11-M	Heat up 1 hr 1 hr, 10 min activation	N_2 H_2	430° to 480°C	200 psig	3 hr	2 hr 455°C 1 hr 180°C	170 psig	3/16 x 3/16" Tablets	No conversion.

CHAPTER V

DISCUSSION OF RESULTS

Several runs were made with each catalyst. The exact conditions for each run are presented in Table VI for the nickel catalyst and Table VII for the molybdena catalyst.

Nickel Catalyst

For the nickel on alumina catalyst several runs were within the range of conditions suggested in Table II. Experimental conditions of 40° to 55°C gas temperature and 3.5 psig for runs 3-N and 5-N were well below recommended temperature and pressure, but certainly within the range suggested. Runs 12-N and 13-N were close to the recommended temperature of 120°C, however, the pressure was 3.5 psig. For all four of these runs the catalyst was visually observed to be active as suggested by color (10). The very small amount of polymerization suggested the polymer was building up on the surface of the catalyst and inhibiting the reaction. A more detailed discussion of each run follows.

For the first four runs with the nickel catalyst, a variety of activation conditions was used to try to establish a method for making an active catalyst. Temperatures of 260°, 330°, and 360°C were used. Oxidation was 1.5 and 2 hours and reduction time ranged from 45 minutes to 3 hours. Based on later measurements, the internal gas temperature was from 20° to 40°C. The primary concern for these runs was that the

temperature be within the range of polymerization conditions. The internal gas temperature established this. For these four runs, the impurity level was reduced by a 3 hour nitrogen purge and a 15 minute ethylene purge. Later measurements showed that this method reduces the impurity level to below 2000 ppm. Of these first runs only Run 3-N gave an active catalyst and detectable conversion. (Active catalyst is explained in the next paragraph). Runs 1-N, 2-N, and 4-N were not active and gave no conversion.

The main object of these first four runs was to observe the catalyst color after activation, as an indication of obtaining the proper catalyst state. References (4, 13, 18, 21) indicated a reduced valence state of +5 for the nickel was favorable to polymerization; therefore, the grey-green (mostly green) mixture of Run 3-N was chosen to be the state for polymerization trials. The green particle represented the +5 valence state and the grey particles were probably the +6 state for the nickel catalyst (10). The actual or preferred valence state is still open to much speculation as stated by Clark (5). Whether +5 or +6 or a combination of the two is the active species is unknown. Several publications support the idea that the active state is an overall average between +6 and +3 (8,5). Molybdeum oxide is more stable as +6. Having both catalysts in the +6 state, reduction to a lower state was the first activation state. Only the colors of the catalysts were used as indications, and no attempt was made to define the exact state of the mixture present.

According to Peters et. al. (15) activation time could be shortened by an increase in pressure. For Run 5-N, the activation time was shortened by eliminating the oxidation and reducing the reduction time

to 40 minutes. The pressure was raised to 200 psig. The catalyst came out active as shown by color. For the polymerization part of the run, the plexiglass reactor tube was replaced with a glass tube and the reactor gas temperature was raised to 55°C. Again polymerization conditions were present, as suggested in Table I. The catalyst was washed with a solvent, but very little (.03 gm per 38 gm catalyst) was recovered.

Conversion was actually measured for only two runs. The catalyst was weighed before polymerization and the weight of the polymers was determined after the washing process to obtain a polymer per gram of catalyst ratio. The amount of conversion for other runs was visually determined to be close to the amount of the weighed runs.

Runs 6-N and 7-N were attempts to use a regenerated form of the catalyst from Run 5-N. The regeneration process consisted of heating to 260°C in nitrogen then reducing for 40 minutes in H_2 for Run 6-N. Run 7-N treatment was oxidation for 2 hours followed by 40 minutes reduction. The desired catalyst color was not obtained for either run. The difficulty of such regeneration has been noted (13). Peters et. al. made the suggestion that a washing-heating cycle was needed, but that the regeneration was not very successful.

On Run 8-N an internal thermocouple was installed to measure the temperature of the ethylene gas inside the system. The chromatograph sampling technique for determination of impurity levels was also employed. For this and the remaining Runs 9-N to 13-N, the impurities level was reduced to the order of 100 ppm via the evacuation procedure. Again, the temperature of polymerization was increased, but there was no effect on the amount of conversion. On this run, the catalyst was a

black-green instead of the grey-green desired.

For Runs 9-N, 10-N, and 11-N the catalyst had the black-green color. A form of nickel hydroxide is reported to be black (10); however, deliberate attempts to form a hydroxide by introducing water under temperatures and pressures similar to those of Runs 9-N to 11-N failed to produce the black particles. Nickel peroxide, which is also inactive, is another black form of the nickel. The polymerization step was carried out for all three runs (9-N to 11-N) and no reaction was noted. The presence of the black particles suggested that the catalyst was not in an active state. The temperature for these three runs was close to the suggested reaction temperature of 120°C (see Table II).

Activation for Run 12-N was at atmospheric pressure and the heat up time was reduced to 35 minutes. The heat up time was also used to reduce the catalyst with H_2. Therefore, the final temperature of 260°C was never achieved. Again, as shown in Table VI, the catalyst came out active. Upon contacting the catalyst with ethylene, the few grey particles of catalyst were observed to turn green. Very low conversion, comparable to that of Runs 3-N and 5-N, resulted.

For Run 13-N, the catalyst was activated with H_2 for 15 minutes and came from the activator with approximately a 50/50 mixture of grey to green particles. Upon beginning the polymerization run, the grey particles were observed to turn green in the first 15 minutes of the run. This change in color indicates that they were further reduced by ethylene.

Molybdena Catalyst

For the molybdena on alumina, Runs 4-M, 5-M, and 11-M were the only three runs to fall outside the range of polymerization conditions as indicated in Table II. Runs 4-M and 5-M were outside suggested catalyst activation conditions and Run 11-M was above recommended polymerization temperature. No polymer formed in these runs.

Runs 1-M through 3-M and 7-M through 9-M indicated there was a wide range of activating conditions for the catalyst. However, a quantitative measure of the effect of activation conditions was not possible because the yield was limited to such very small amounts. Runs 2-M and 8-M indicated that one effect of increasing temperature was an apparent lower molecular weight product. Conversion for the two runs did not change, indicating temperature was not the single controlling factor in the process. Runs 2-M and 3-M showed no variation in quantity of product upon change in impurities level from 2000 ppm to the order of 100 ppm.

For molybdena, the reported activation conditions seemed to be more accurate. For each run, a consistent color change was observed for a wide range of conditions of the activation step. For the first and second runs with the molybdena, the impurity level was reduced to a level below 2000 ppm by purging with nitrogen for 3 hours prior to running and also purging with ethylene for 15 minutes. The molybdena catalyst was observed to change color from mostly white and some grey, to a mixture of light browns and some white on activation. The color change corresponded to the valence state thought to be most active (+5). Molybdenum in the +6 state corresponds to a color of greyish-white, while the +5 state corresponds to light to medium dark brown (9).

After a reaction time of three hours for Run 1-M, the catalyst was noted to have a distinct petroleum odor. Upon washing with chloroform and benzene, a product weight of approximately .03 gm per 38 gm catalyst was measured. After drying, the polymer was observed to have a wax like nature. The gas temperature on Run 1-M was about 90° to 100°C.

The activation time for the second run was shortened by 15 minutes; however, the other conditions remained approximately the same as those for the first run. For this second run, the amount of polymer recovered was approximately identical to the first run. The third run was a repeat of the first two, the main variation being a few minutes activation time for the catalyst and the impurities level was reduced to the order of 100 ppm. The remaining runs were also made at impurities levels on the order of 100 ppm or lower. The first three runs indicated the activity of the catalyst was not affected significantly by variations in activation time (over 35 to 60 minutes) nor the impurities level over a range of 30 to 2000 ppm. That is, the amount of conversion was the same for all three runs. If some factor other than temperature and impurities was inhibiting the reaction, the variation in activation time and impurity level might not have been observed due to the low conversion caused by the limiting factor, i.e., the effect of changes in temperature and impurities could have been masked by another factor.

Run 4-M was used to make sure the small conversions being recorded were not just residue from the catalyst itself. Run 4-M also indicated that some reduction was needed. The activation for the fourth Run consisted only of heating to 455°C for two hours with dry air passing over the catalyst but no subsequent H_2 reduction. An in-line air dryer was used to insure no water was present in the air. Using air at this tem-

perature for the activation process should have oxidized the catalyst to its highest possible valence state. Indeed, the catalyst was almost solid white, corresponding to the +6 state. The temperature of the reaction gas for Run 4-M was slightly higher for the 3 hours of reaction time. The catalyst had no strong petroleum smell, and after washing in chloroform and then evaporation there was no product residue.

Run 5-M was an investigation of the other extreme for the catalyst. The catalyst was reduced for four hours in a hydrogen atmosphere with no preceding oxidation step. The treated catalyst was a medium to dark brown color, corresponding to the reduced +5 state. Actually lower valence (+3,+1) states may have been present; however, based on color only the +5 state was confirmed. Reaction temperature for Run 5-M was some 60°C higher than for the previous four runs. After washing the reacted catalyst, no conversion was detected.

For Runs 6-M through 9-M, the internal temperature was held at approximately 175°C. For Run 6-M the reduction time for the catalyst was 15 minutes. The variation in reduction times was used to obtain varying mixtures of the different valence states. When the catalyst from Run 6-M was boiled in the solvents, the amount of product obtained upon evaporation was approximately the same as that from Runs 1-M through 3-M. However, the product for Run 6-M was noticeably "greasier" than the hard wax of the first three. This apparent decrease in molecular weight with increase in temperature has been reported (12).

For Runs 6-M, 7-M, and 8-M the conditions were the same except for H_2 reduction, which varied from 5 to 35 minutes. The resultant polymer formation was essentially the same in these three runs. About .03 grams of polymer per 38 grams of catalyst were obtained in each run. Run 8-M

should be compared to Run 2-M for the effect of temperature on the reaction, 90° and 174°C respectively. The primary difference was not the amount of product, but the apparent decrease in molecular weight upon increasing temperature.

Catalyst size was changed from the 20 to 48 mesh particles to 1/8" by 1/8" pellets for Run 9-M. Reaction temperature was also lower than the previous four runs. The product, however, was approximately the same as Runs 6-M to 8-M.

Runs 10-M and 11-M were made in the activator bomb. For the Run 10-M, the catalyst was reduced for one hour at 430° to 480°C, temperature was allowed to decreased to about 150°C, and the activator was then maintained with ethylene at 165 psig for 3 hours. At the end of the reaction time the catalyst had to be scraped from the tube. Upon boiling in chloroform, benzene, and xylene, 1.7 grams of greases and waxes were removed. Another gram of high molecular weight polyethylene was removed with trichlorobenzene.

Run 11-M was a repeat of Run 10-M with the exception of catalyst size (1/8" x 1/8") and reaction temperature (2 hours at 455°C). No product was observed probably because this temperature is above the suggested range for polymerization and also above the point at which polyethylene will vaporize.

Except for pressure, several runs with the molybdena met the suggested conditions for polymerization. Run 10-M for the molybdena confirmed the need for pressure. The conditions were approximately the same as Runs 1-M and 8-M giving clear indication of the importance of pressure. The 165 psig used for Run 10-M was well below the suggested condition of 1100 psig. This lower pressure therefore represents some

real possibilities for economizing the polymerization process and 165 psig is at least equivalent to present commercial processes.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The polymerization was not affected to a great degree at moderate conditions (18 psia, 170°C) using the nickel catalyst. The nickel catalyst seemed extremely sensitive to the activation conditions. Reaction did occur for the low pressure, but little polymer was obtained. Temperature and impurities level were not solely responsible for the low conversion.

The molybdena catalyst appears to be easily activated for a range of conditions, within the specified limits. The molybdena catalyst showed that the polymerization did take place at atmospheric pressure although at very low conversion. One effect of temperature was to make the molecular weight of the products lower. The next to last run for the molybdena was an indication of one of the possible variables to be investigated in finding good conversion conditions. The higher pressure of the last runs would indicate a mass transfer step as a possible controlling factor in the polymerization. This was the conclusion reached for the nickel catalyst also.

Recommendations

There are possibilities for an improved polymerization process and the gas phase project should be continued.

The nickel catalyst did not appear to be a promising catalyst at the moderate conditions and a detailed study of the active valence state should be made before further polymerization studies. The molybdena on alumina should be the catalyst used in the next study. Some specific recommendations for the next project on low pressure, gas phase polymerization are as follows:

1. Build another flow type system similar to the one of this study with the added capability of operating at pressures as as high as 500 psig.
2. Establish a precise method for measuring the conversion vs. amount of catalyst used.
3. Determine the effect of pressure from 100 psig to 500 psig.
4. Try to regenerate the molybdena catalyst for recycle use.
5. Using conversion per gram of catalyst and the possible number of recycle times for the catalyst, rough out some economics for a commercial venture.

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APPENDIX

CHROMATOGRAPH OPERATION AND CALCULATION OF AMOUNTS OF IMPURITIES

CHROMATOGRAPH OPERATION AND CALCULATIONS OF AMOUNTS OF IMPURITIES

Chromatograph Operation

An F&M Scientific Corporation, Model 500 chromatograph was used. The chromatograph was operated with the following list of control positions.

1. Switch for temperature programmer -- off
2. Manual temperature set -- on
3. Temperature limit -- 300°C
4. Temperature selector -- block
5. Column heater switch -- off
6. Master power switch -- on
7. Bridge power -- on
8. Milliamperes gage -- 150
9. Column blower -- off
10. Injection port heater -- on
11. Rheostat to control injection port -- 30
12. Temperature controller for injection port -- 120°C
13. Carrier gas control valve -- full open (35 cc per min.)

A Minneapolis-Honeywell, Model Y15307856-01-05-0-000-615-07-009 recorder was used to record the output signal of the chromatograph. Chart speed was 1.5 inches per minute.

The chromatograph was modified by installing a 7 Port, Manual, Microtek valve. The valve eliminated the possibility of injecting air with the sample. For the sample loop on the valve a 51" length of 1/8" copper tubing was used (2 cm^3 volume). The value was installed

between the helium control valve and the detector block such that a constant flow of helium passed through the valve. The column was packed with Porapak-S, a commercial packing made by Waters and Associates.

The chromatograph was turned on and helium was allowed to flow through the system for 24 hours. This allowed the instruments to warm up and impurities to be carried out of the column. Next the sample loop was purged for one minute with the reaction gas and a sample was injected into the system. The recorder was turned on and the initial attenuation was set for the first peak. After the first peak came out on the recorder the attenuation was reset for the second peak. The attenuator was returned to its initial setting and the sample valve was returned to its original position ready for another sample.

The amount of ethylene and impurities was determined from a simple ratio of areas on the chromatogram curves. The exact impurity level was not determined; however, the method used would be a conservative, but adequate, estimate of the amount of impurities present. The three chromatograms represent the process of reducing the impurities level in preparation for a polymerization run.

Calculations

Chromatogram 1 -- after 5 evacuations

Small Peak Area -- (47 squares) x (attenuation of 16) = 1162

Large Peak Area -- (375 squares) x (attenuation of 128) = 48,000

Impurity level = 1162/49.162 = 24,000 ppm

Chromatogram 2 -- after 10 evacuations

Small Peak Area -- (41 squares) x (attenuation of 4) = 164

Large Peak Area -- (370 squares) x (attenuation of 128) = 47,360

Impurity level = 164/47.526 = 3400 ppm

Chromatogram 3 -- after 10 evacuations and five minute purge

Small Peak Area -- (1.5 squares) x (attenuation of 1) = 1.5

Large Peak Area -- (353 squares) x (attenuation of 128) = 45.184

Impurity level = 1.5/45,185 = 33 ppm

Figures 6, 7 and 8 show corresponding chromatograms.

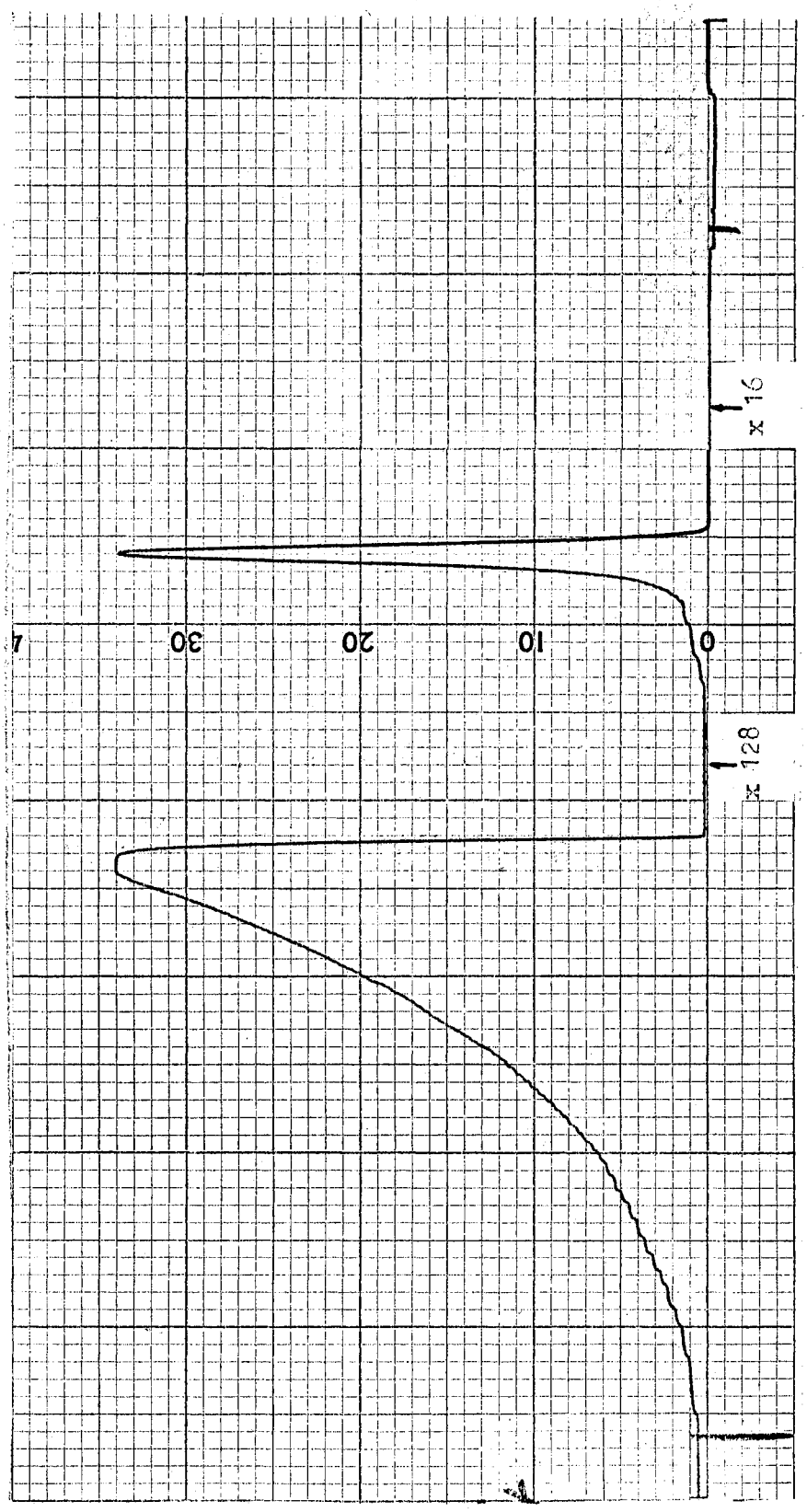

Figure 6. Chromatogram 1: After 5 Evacuations

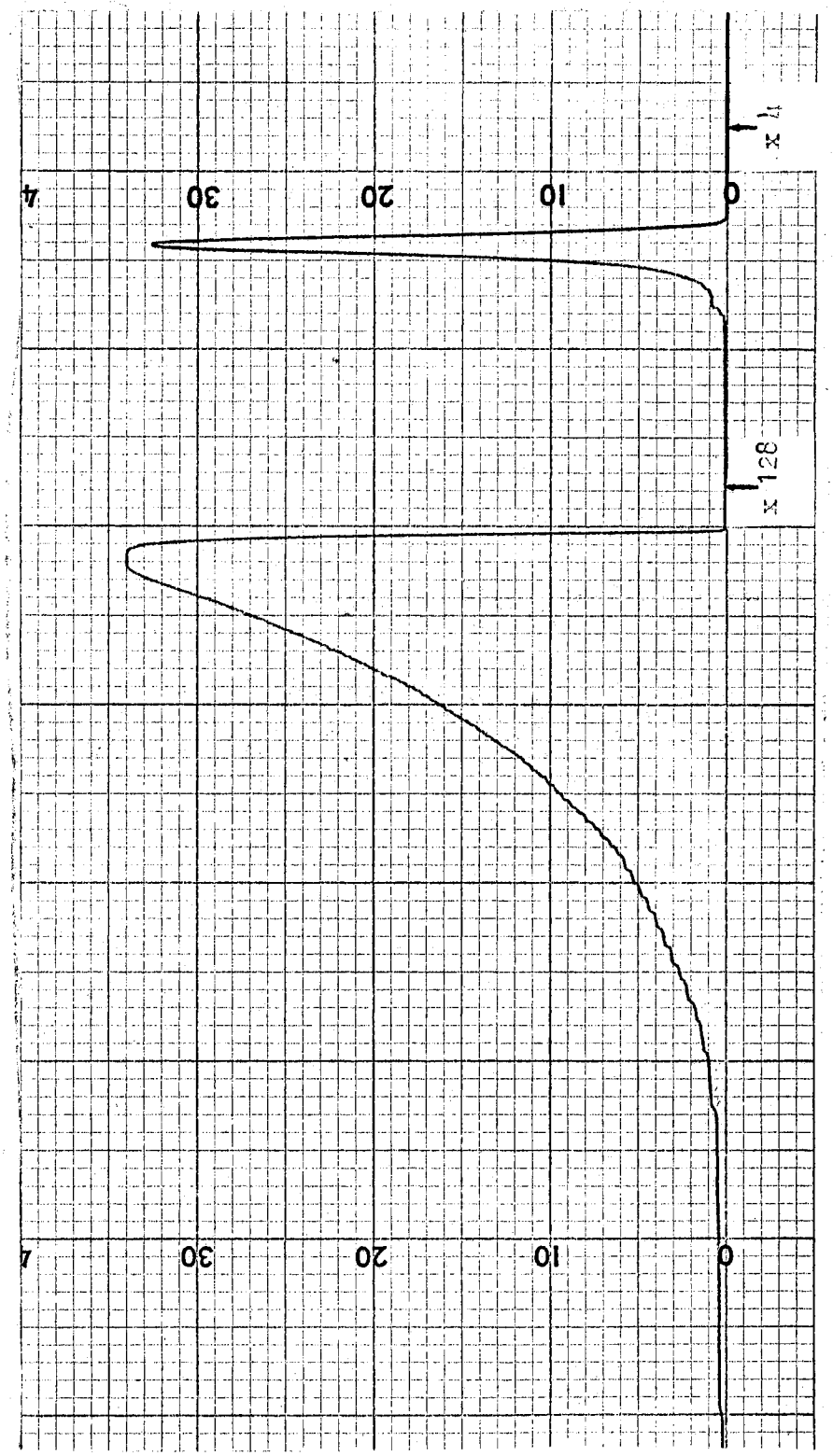

Figure 7. Chromatogram 2: After 10 Evacuations

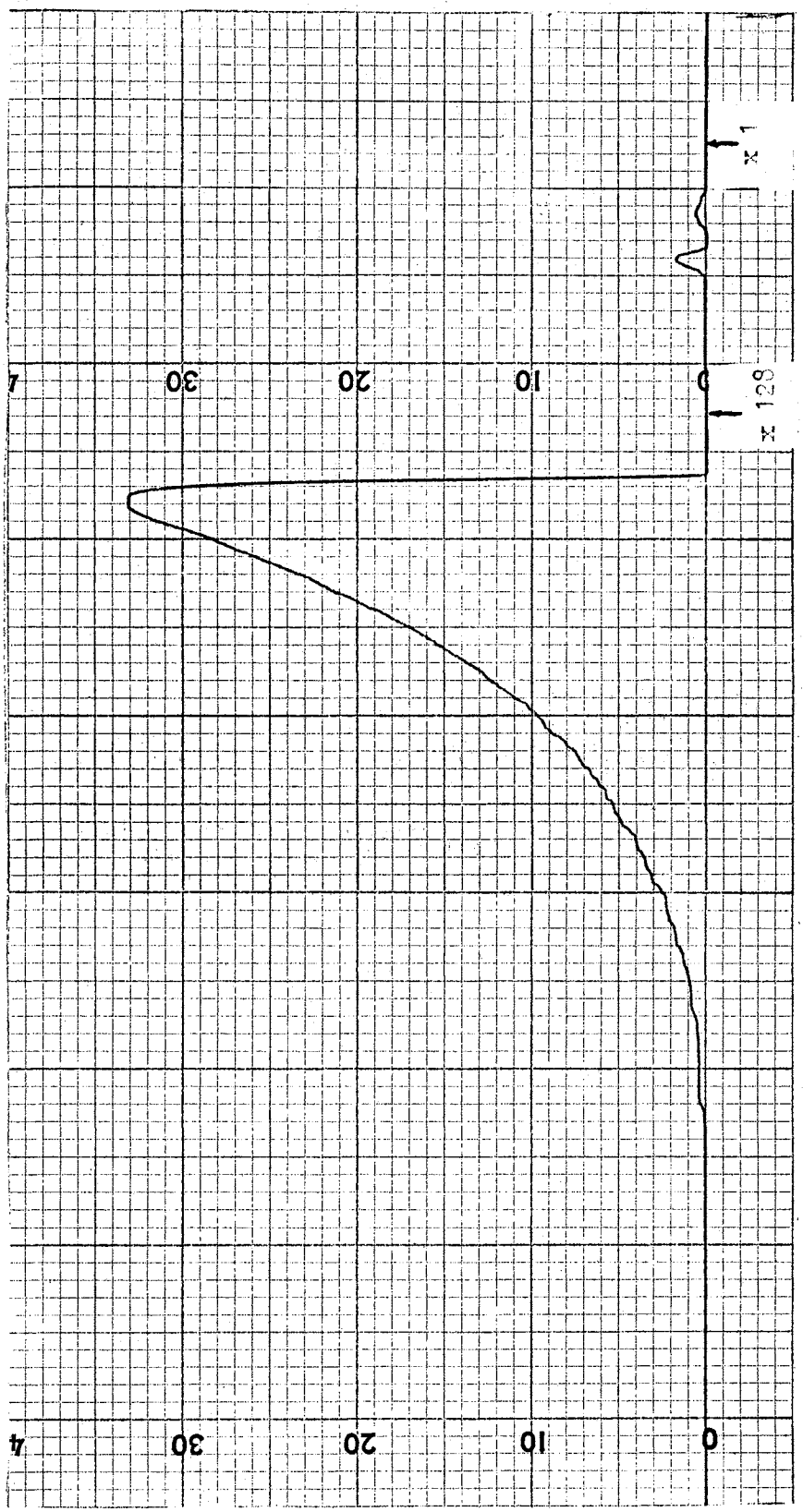

Figure 8: Chromatogram 3: After 10 Evacuations and 5 Minute Purge

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